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## PROCEEDINGS

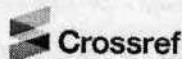
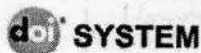
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## Effect of The Use of Environmentally Friendly Tanner Material On the Process of Tannery of Puffer Fish (*Arothron Reticularis*) Skin Against Physical Test and Histology of Skin

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### Abstract

One of the results of marine fauna in Indonesia is Pufferfish fish. Pufferfish fish is unique in its body surface covered with spikes and a fish species that are toxic, that the fish utilization is not maximized. On the other hand, the skin can be used as alternative raw materials for the tanning industry given the limitations of raw leather raw material land animals. The aim of this study was to process puffer fish skin which are avoided as toxic to be useful to society, test technical methods of environmental friendly tanning, examines the factors of the results of physical tests of Tensile Strength, Power Stretch and Resilience of Tear, and examine the structure of the specification from pufferfish skin with histological structure of the skin in a light microscope. This study was using skin of Pufferfish were 100 pieces of puffer fish skin taken from Rembang, Central Java of tanned using environmentally friendly tanning materials covering mimosa, quebracho and tare up into crust skin of Pufferfish. Treatment was using variations in the concentration of environmentally-friendly tanning materials used were 16%, 18% and 20%. The use of tanning mimosa 16% shows the value of Tensile Strength and the highest Tear Strength is 1902,873 N / cm<sup>2</sup> and 509,812 N / cm and elongation values and the lowest enervation is amounting to 92.407% and 2,84mm. Quebracho tanning material use was 16% showed the highest tensile strength that is equal to 1859,952 N / cm<sup>2</sup> and elongation values and the lowest enervation is 103.12% and 2.44mm, the use of tanning quebracho 20% shows the highest value of tear strength equal to 402.299 N / cm. The use of tanning Tara 18% shows the highest value of tensile strength and tear strength is 1354,193 N / cm<sup>2</sup> and 262,392 N / cm, the use of tanning tara 16% showed the lowest enervation value equal to 3.4mm and the use of tanning tara 20 % indicate elongation value equal to 65.06%.

**Keywords:** green chemical; puffer fish; physical test

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### INTRODUCTION

In Indonesia, the leather tanning industry uses raw materials derived from animal leathers such as goats, sheep, cows, buffalo and reptiles has been growing rapidly a produced finished product such as shoes, bags and jackets which have quality is not inferior to foreign-made product. However, the tanning industry that uses raw materials of fish leather are still few in number. One of the way that can be done as an alternative is the use of fish leather as a raw material tannery. Skin of the fish can be potentially developed but the movement is very slow. The utilization of the fish skin tannin does not only add the value of the fish leather wastes, but it all can be an alternative in fulfilling the need of leather as the raw materials in the leather jacket industry in Indonesia that has been applied to the manufacture of leather-based products, such as handbags, shoes, slippers. Nowadays, most of the world's leather tanned with chromium (III)

sulphate, which is a consequence of the ease of the provide feat of product use, and very satisfying characteristics of leather produced. However, the mineral tanning also contributes to the problem of environmental pollution, especially in developing countries. Thus, the necessary non-mineral tanning process environmentally friendly in the manufacture of leather. Vegetable tanning (condensed vegetable tannages) such as mimosa, quebracho, and Gambir is non mineral tanning materials produced from renewable natural resources and are environmentally friendly [1].

The purpose of this study is to process the leather of puffer fish which are avoided by the society because of its toxic, and make it beneficial for the community, assess the technical methods of tanning environmentally friendly, examine the factors of the physical tests results of the Tensile Strength, Power Stretch and Resilience Sobek, and examine the structure of the specification of leather puffer fish with skin histological structure in light microscopy and electron microscopy.

There are some similar researches related to the leather tanning of rays, tilapia and snapper, but the utilization of the leather of the poisoned fish is still in an opinion only. Puffer fish skin is an attractive leather with prickly but very unpopular because of toxic indicated. The process was generally similar to the Tannery which has primarily been carried out on a stingray, snapper or tilapia. The difference is the leather of puffer fish has thorn on its leather which is a combination of hair-like keratin and collagen. So, there is a special feature on this skin. It is deepening the histological structure of each stage of the tanning process to look at the leather physical properties also has not been done.

#### MATERIALS AND METHODS

The materials used in the study were 100 pieces of puffer fish skin taken from Rembang, Central Java. The skin of puffer fish was taken randomly. The materials used in this study are: Water; Wetting agent (Piramit ML); Chalk; Oropon OR; Formic acid; Vegetable tanning materials (mimosa, quebracho, tara), ZA; Petroleum sulfonate (Tannit LSW); Hydrochloric acid; Antiseptic (Previtol CR); Sodium bicarbonate; Syntan; Formalin Sodium hydroxide; Alcohol 96%; Absolute alcohol; Paraffin; toluene; Ice Cube; ethanol; Hematocilin Haris; eosin; Dry tissue; Ewitt solution.

This research was conducted through six (6) stages, namely: Tanning with three ingredients tanner environmentally friendly, namely Mimosa, Quebracho and Acacia / Tara, the concentration of each ingredient tanner environmentally friendly 16, 18 and 20%, physical testing skin results tanning, and structure Histology skin. In the making of this histology preparation, the tissue of fish leather which would be observed was pickled by using formalin, then it was sliced thin (with a thickness of few micron), sticked up to the glass object, colored, and then covered by the glass cover [2]. For the assessment of tensile strength was conducted based on the Indonesia standard of SNI 06-1795 -1990 [3].

The research was conducted from June 2015 to August 2015. The research was conducted in the laboratory of Microbiology and enzymes, Waste Laboratory, Laboratory Finishing Polytechnic ATK Yogyakarta. Laboratory testing in Patologi Anatomy of Medicine, Laboratory of Agricultural Technology UGM, LPPT UGM, and the Center for Skin Rubber and Plastic Yogyakarta.

#### RESULT AND DISCUSSION

##### Histological Observation Result of Puffer Fish Skin

In Figure 1, it appears to differences in levels of vegetable tanning materials 16%, 18% and 20% where the histological structure seems a higher level of mimosa apparent collagen fibers seem tenuous [4]. Suggest that naturally, the structure of fish skin dermis can make its tensile strength is quite high due to the parallel trans structure. The dermis is composed and organized as parallel fiber layers which tend to form an angle (helically oriented) in the opposite direction. Figure 2 shows the results of histological structure observation using a puffer fish leather with Quebracho as a tanner. The more tightly the collagen structure, it will affect tensile strength and elongation leather on physical testing.

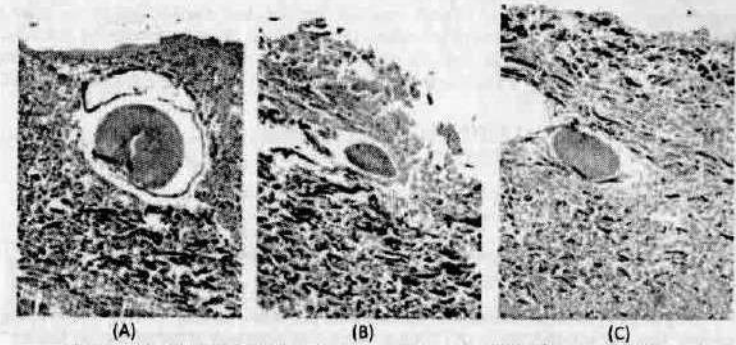


Fig 1: (A) The Microstructure thickness of the puffer fish leather with Mimosa 16% staining Malory 40x magnification; (B) The microstructure thickness of the puffer fish leather grading 18% of Mimosa staining Malory 40x magnification; (C) The Microstructure thickness of the puffer fish leather grading 20% of Mimosa Malory coloring 40x magnification

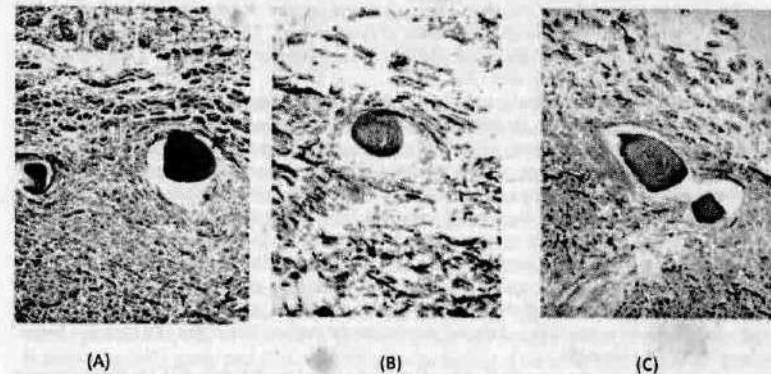


Fig 2: (A) The microstructure thickness of the puffer fish leather with higher levels of staining Malory Quebracho of 16% with 40x Magnification; (B) The microstructure thickness of the puffer fish leather grading 18% of Quebracho staining Malory 40x magnification; (C) The microstructure thickness of the puffer fish leather grading 20% of Quebracho Malory coloring 40x magnification

Figure 3 shows the microstructure of puffer fish leather by using Tara. In Figure 3a shows the collagen fibers at a concentration of 16% and 20% looks tenuous, while at a concentration of 18% looks compact. This shows that at concentrations of 20% led to a rift back in its histological structure. This can occur due to the inclusion or dependent tanning material into protein molecules making up the skin that result in the formation of crosslinks between tanning material with a polypeptide chain determine the level of physical strength of leather. Tear strength equivalent to a tensile strength of leather and inversely proportional to the elongation.



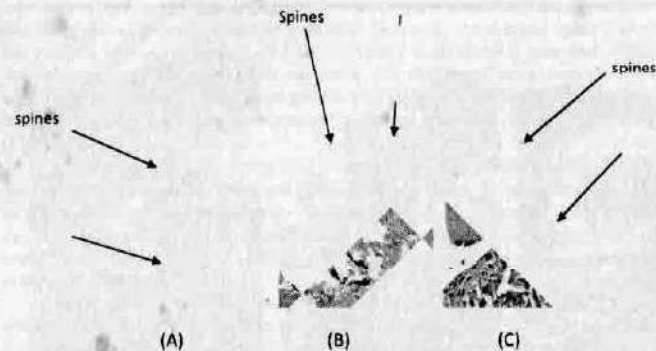


Fig 3: (A) The microstructure thickness of the pufferfish grading 16% of Tara staining Malory Tara 40x magnification; (B) The microstructure thickness of the puffer fish leather grading 18% of Tara staining Malory 40x magnification; (C) The microstructure thickness of the pufferfish leather grading 20% of Tara coloring Malory 40x magnification.

### Results of Physical Strength of Puffer Fish Leather Test

Tanning goal is to transform raw skin easily damaged by the microorganisms, physical and chemical activities into the skin more resistant to these effects. The principle of tanning is the inclusion of certain material (tanning substances) in the skin fiber and causes a chemical bond between tanning substances and skin fiber.

Leather has the physical properties and chemical composition that is different [5]. Physical strength according to Roddy, [6] is the power to influence the environment, among others, the effect of storage power, physical strength can be measured quantitatively, e.g. tensile strength, elongation, temperature wrinkles and rigidity. The physical strength according to Tuck [7] correlated with tissue structure and the levels of chemicals on the leather, so that the amount of physical strength of the leather can be expected from the tissue structure and the levels of chemicals leather. the tanning process, there are some steps to go through. First step is the reaction between hydroxyl groups in vegetable tannin and collagen structure. Second is the bound reaction from tanning and other substance molecules until all empty spaces in the collagen chains are filled completely during tanning processes, with osmotic swelling of fibril structure due to acid surrounding. Tanning results can be perfect if collagen can absorb a half of the tanning substances used.

Table 1 shows the physical strength test results of puffer fish skin, including tensile strength, elongation, and tear strength. This shows that there are differences in tensile strength, elongation, and tear strength, on the vegetable materials group. Treatment was using variations in the concentration of environmentally-friendly tanning materials used were 16%, 18% and 20%. The use of tanning mimosa 16% shows the value of Tensile Strength and the highest Tear Strength is 1902,873 N / cm<sup>2</sup> and 509,812 N / cm and elongation values and the lowest enervation is amounting to 92.407% and 2.84mm. Quebracho tanning material use was 16% showed the highest tensile strength that is equal to 1859,952 N / cm<sup>2</sup> and elongation values and the lowest enervation is 103.12% and 2.44mm. the use of tanning quebracho 20% shows the highest value of tear strength equal to 402.299 N / cm. The use of tanning Tara 18% shows the highest value of tensile strength and tear strength is 1354,193 N / cm<sup>2</sup> and 262,392 N / cm, the use of tanning tara 16% showed the lowest enervation value equal to 3.4mm and the use of tanning tara 20% indicate elongation value equal to 65.06%. One important factor influencing the physical character of tanned leather is the raw skin structure. Tensile strength is one element that needs to consider in assessing leather quality. It is alleged that the effect of tanning substances put into the skin is very influential on the physical strength of skin. During the

tanning process, there are some steps to go through. First step is the reaction between hydroxyl groups in vegetable tannin and collagen structure. Second is the bound reaction from tanning and other substance molecules until all empty spaces in the collagen chains are filled completely during tanning processes, with osmotic swelling of fibril structure due to acid surrounding. Tanning results can be perfect if collagen can absorb a half of the tanning substances used [8].

Table 1: Physical Test Results

Vegetable Materials	Physical Tests Results			
	Tensile Strength (N/cm <sup>2</sup> )	Elongation (%)	Tear Strength (N/cm)	
Mimosa	16%	1902.873	92.407	509.812
	18%	1410.026	101.817	213.620
	20%	1384.365	114.503	321.951
Quebracho	16%	1859.952	103.120	337.609
	18%	1357.201	112.517	376.802
	20%	1314.444	119.297	402.299
Tara	16%	1108.146	93.617	217.935
	18%	1354.193	74.677	262.392
	20%	1099.254	65.060	145.857

The research of fish skin tanning which is familiar in pubic are such as snapper, tilapia, or stingray as the most consumed meat. [9] state that the use of vegetable tanning material concentration (mimosa) as the most excellent of the physical properties quality of red snapper tanned skin is the tanner ingredient concentration of 20%. Moreover, Alifindo (2009) [10] states that the concentration of mimosa 15% gives the most influence on both the tensile strength and tear strength, while mimosa concentration of 5% gives the most influence both the tensile strength of the tanning tuna. Sharphouse (1971) [11], too much mimosa will cause the accumulation of mimosa in the skin which can reduce the strength of the skin, since the skin becomes brittle. The low elongation obtained with mimosa tannin is as a result of the mimosa tannin that change a single fiber into a compact structure of the skin. The empty skin structure due to protein loss will be filled by a hydroxyl group of tanning substance, where hydroxyl is bound to the NH<sub>3</sub> group and COO of collagen structure. [12] Tanning with vegetable, collagen parts that can react with the tanning agent are peptide side chains that are free, so it is able to form hydrogen bonds with the active group structure contained in the tanning substances. This condition will cause a state of "case hardening" (dryness of the surface) which causes stiffness of the skin. Mimosa is a source of tannin with high astringent character.

Table 2: Assays Tanin

Tanning materials	Mimosa	Quebracho	Tara
Beginning (g/l)	67.81	59.09	47.82
Ending (g/l)	19.80	16.77	10.13
Absorbing (%)	70.801	71.619	78.816

In Table 2, it can be seen that tannin levels seen early and after tanning decline means that the tannins absorbed into the skin. Tanner substance must penetrate the leather from the surface of the leather and of the meat fibers woven into the structure, until the free water between the fibers of the leather surface.



The utilization of the fishery products as the source for tanning industry still faces some obstacles and problems; one of which is because the fishery products are rapidly decaying commodities including fish skin. Chemical composition and physical structure of the fish skin is different from the skin of land animals. Fish skin is more susceptible to damage. Consequently, the fish skins which can be tanned must be obtained from fish with excellent freshness. Thus, the fish handling should be done in a good method. Likewise, fish skin that has been removed from the body of the fish requires good handling and should be processed as quickly as possible. Scarcity of supply in the fish skin for tanning industry mainly lies in the difficulty of getting a decent quality of fish skin for tanning.

### CONCLUSION

1. The observations result of the Histological structure shows the use of Mimosa of a concentration of 16%; 18% and 20% biodegradable collagen fiber structure, it is the same as the use of tanning quebracho. The use of Tara Tanner showed concentrations of 16% and 20% collagen concentration biodegradable and 18% fibers compact.
2. The use of tanning mimosa 16% shows the value of the highest of the Tensile Strength and Tear Strength at 1902,873 N / cm<sup>2</sup> and 509 812 N / cm and the lowest elongation values and enervation at 92.407% and 2.84mm.
3. The use of tanning materials of quebracho 16% shows the highest tensile strength that is equal to 1859,952 N / cm<sup>2</sup> and the lowest elongation values and enervation at 103.12% and 2.44mm, the use of tanning quebracho 20% shows the value of the highest tear strength at 402.299N / cm.
4. The use of Tara tanner 18% shows the value of the highest tensile strength and tear strength at 1354,193 N / cm<sup>2</sup> and 262 392 N / cm, the use of tanning tara 16% shows the value of the lowest enervation at 3.4mm and the use of tanning tara 20 % shows the value of the lowest elongation at 65.06%.
5. The result shows the levels of tannin solution usage of mimosa, quebracho and tara before playing with puffer fish skin showed 67.81 g / l; 59.09 g / l and 47.82 g / l decreased after playing together with the leather of puffer fish is 19.8 g / l; 16.77 g / l and 10, 13 g / l and it shows the level of tannin / tannic substance is absorbed each ingredient on the skin tanning pufferfish. On mimosa tanning materials absorbed by 70.801%, 71.619% of quebracho absorbed and Tara absorbed by 78.816%.

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